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ASPECTS OF ARYNE CHEMISTRY—II[1]

THE REACTION BETWEEN ISOSAFROLE AND DIAZOTISED ANTHRANILIC ACID UNDER DIFFERENT CONDITIONS[2]

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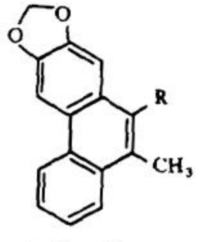
Abstract—The main products derived from the interaction of isosafrole with either benzenediazonium-2-carboxylate, or with anthranilic acid and amyl nitrite, are the phenanthrene derivatives expected from a Diels–Alder addition involving benzyne as an intermediate. With benzenediazonium-2-carboxylate hydrochloride and isosafrole, however, the chief product is *trans*-3-(3′,4′-methylenedioxyphenyl)-4-methyl-3,4-dihydroisocoumarin. The reasons for this difference in behaviour are discussed.

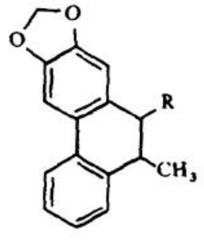
IN PART I of this series,[1] we described a synthesis of phenanthrene derivatives that involved the addition of benzyne, generated by the aprotic diazotisation of anthranilic acid,[3] to styrene and phenylacetylene derivatives. Since then benzyne has been added to styrene,[4] and to α-methylstyrene.[5] The products in the latter case were 9-methyl- and 9-benzylphenanthrenes. Tetrafluorobenzyne has been reacted with styrene to give[6] 1,2,3,4-tetrafluoro-9,10-dihydrophenanthrene and this reaction has been examined in more detail by Heaney *et al.*[7]

One of the major by-products in our reaction was acridone, formed presumably by cycloaddition of benzyne to excess of anthranilic acid. In an effort to improve yields of phenanthrenes, we have now examined different methods for the generation of benzyne. The use of benzenediazonium-2-carboxylate[8] as a benzyne precursor avoids acridone formation, but because this is potentially hazardous, we selected instead the benzenediazonium-2-carboxylate hydrochloride[9] method for study. The results obtained with isosafrole as benzyne acceptor were so different from our previous[1] ones that we undertook a careful examination of the products obtained by generating benzyne from anthranilic acid under all three sets of conditions.

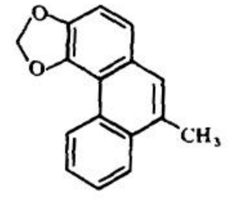
Benzenediazonium-2-carboxylate hydrochloride was reacted with isosafrole in boiling acetonitrile; after removal of solvent, acidic material, and unchanged isosafrole, the product was chromatographed over silica gel. Nine compounds were isolated and characterised. The results are summarized in Table 1. The UV spectra of the 2,3-methylenedioxyphenanthrenes (**1a** and **1b**) are sufficiently different from the spectra of the 3,4-methylenedioxyphenanthrenes (**3** and **4**) for a distinction to be made. The structure of **2a** follows from the fact that dehydrogenation with 10% Pd/C in xylene occurs to yield **1a**, identical with an authentic[1] specimen. The UV and the mass spectrum of **2b** suggested a 9,10-dihydrophenanthrene that differs from **2a** by an additional Ph group. The NMR spectrum (measured in $CDCl_3$ solution with TMS as an internal reference [Fig. 1a] clearly shows that this phenyl group is located at C_{10}; the one proton doublet ($J = 4{\cdot}0$ Hz) at $3{\cdot}86\ \delta$ is assigned to the C_{10} proton, whilst the



1a: R = H
1b: R = Ph



2a: R = H
2b: R = Ph



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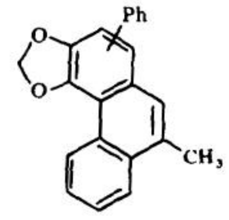

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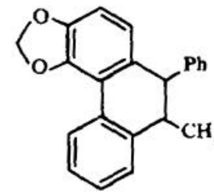

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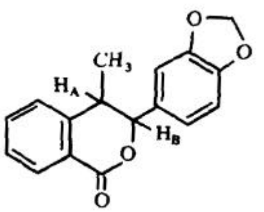
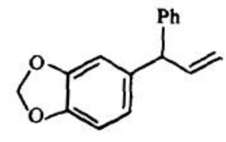


6: H_A, H_B cis
7: H_A, H_B trans



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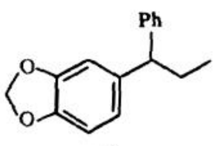

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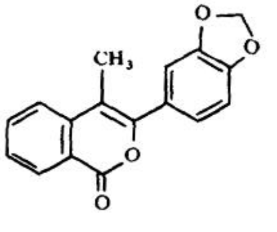

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TABLE 1. PRODUCTS DERIVED FROM ISOSAFROLE

Compound No.	Method* of Benzyne Formation			
	I % yield†	II % yield†	III % yield†	
			a	b
1a	0·8	17·1	5·3	3·9
1b	—	—	—	0·5
2a	1·4	0·1	trace	—
2b	1·1	1·2	0·4	13·3
3	1·2	8·1	3·2	1·0
4	0·4	—	—	—
5	0·1	—	—	1·6
6	0·7	—	—	—
7	9·5	—	—	—
8	0·4	2·8	0·9	2·3

* Method I: Benzenediazonium-2-carboxylate hydrochloride
Method II: Aprotic diazotisation
Method III: Benzenediazonium-2-carboxylate, (a) at room temperature; (b) in boiling acetonitirile
† based on isosafrole consumed

one proton multiplet at 3·02–3·30 δ arises from the C_9-proton. The C_9-Me group absorbs at 1·23 δ as a doublet ($J = 7$ Hz). Dehydrogenation of **2b** was eventually achieved with chloranil, or better with tetrachloro-o-benzoquinone, yielding **1b**, whose NMR spectrum, when compared with that of **1a** (Fig 2) indicated that the methylenedioxy group is located at C_2, C_3. The assignments of protons in the aromatic regions of these spectra agree with some reported previously.[10]

Since the C_9-Me group of **1b** absorbs as a singlet at 2·34 δ, there cannot be a proton at C_{10}. The Me absorption of **1a** at 2·64 δ appears as a doublet ($J = 1·0$ Hz).

The UV spectra of **3** and **4** are similar, and their mass spectra indicated that **4** contains a phenyl group more than **3**. However, that **4** is a 3,4-methylenedioxy-9-methylphenanthrene, unsubstituted at C_{10} is evident from a comparison of the NMR spectra of **3** and **4** (Fig 3). Thus, the C_9-Me absorptions at 2·50 δ in **4** and at 2·60 δ in **3** both appear as doublets ($J = 1·0$ Hz) and ($J = 1·1$ Hz) respectively. Furthermore, the presence of an AB quartet at 7·31, 7·23 and 7·13, 7·05 δ ($J = 8$ Hz) in the spectrum of **3**, assigned to the C_1 and C_2 protons, and the absence of this quartet from the spectrum of **4** suggests that the Ph group in **4** is located at either C_1 or C_2. It has not been possible to distinguish between these alternatives.

The molecular formula ($C_{22}H_{18}O_2$) of **5** was established by high resolution mass spectrometry. The mass spectrum is very similar to that of **2b**. The NMR spectrum compared with that of **2b** (Fig 1b) shows that both are 9-methyl-10-phenyl-9,10-dihydrophenanthrenes. Since **2b** is known to be the 2,3-methylenedioxy derivative, it follows that **5** must be 3,4-methylenedioxy-9-methyl-10-phenyl-9,10-dihydrophenanthrene. In accord with this structure is the presence of an AB quartet at 6·74,

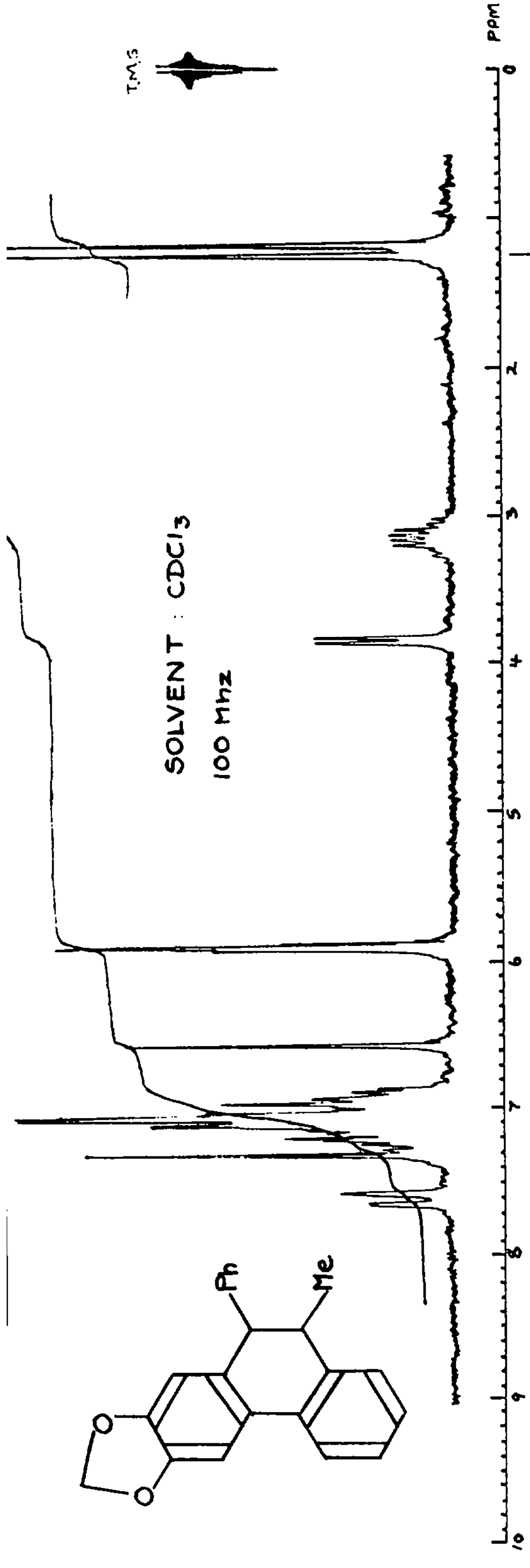
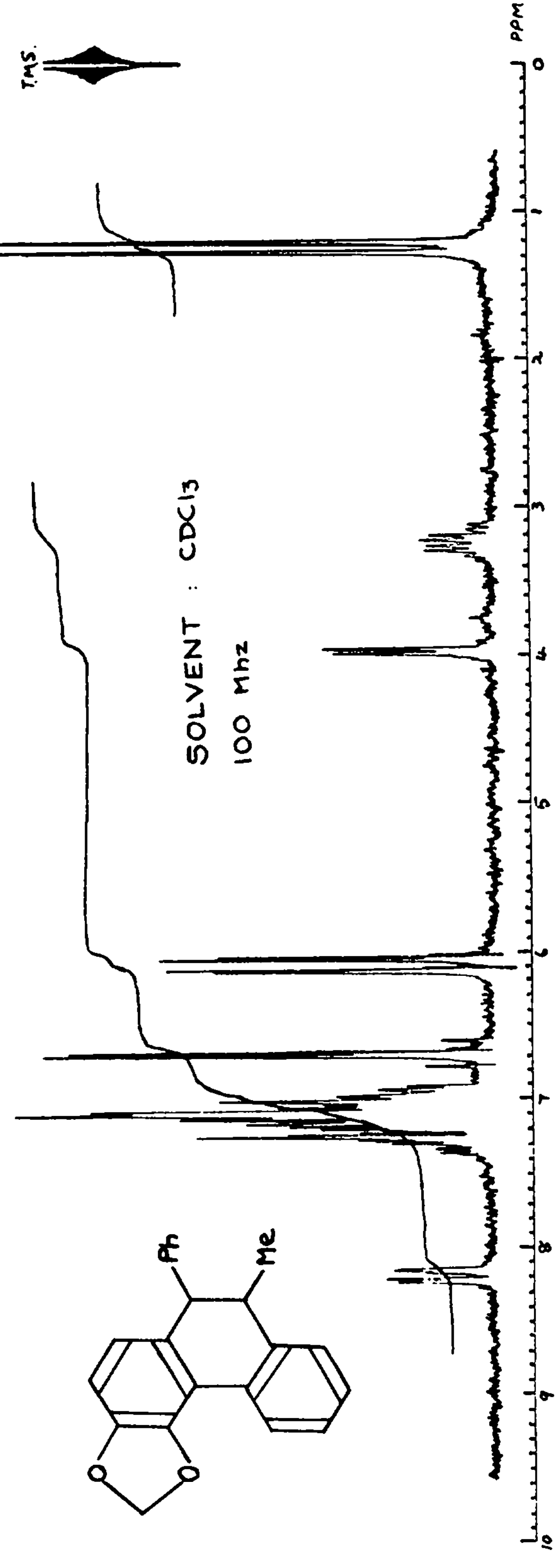

T.M.S
SOLVENT : CDCl3
100 Mhz
Ph
Me
PPM
0
1
2
3
4
5
6
7
8
9
10

FIG. 1A.


T.M.S.
SOLVENT : CDCl3
100 Mhz
Ph
Me
PPM
0
1
2
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5
6
7
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9
10

FIG. 1B.

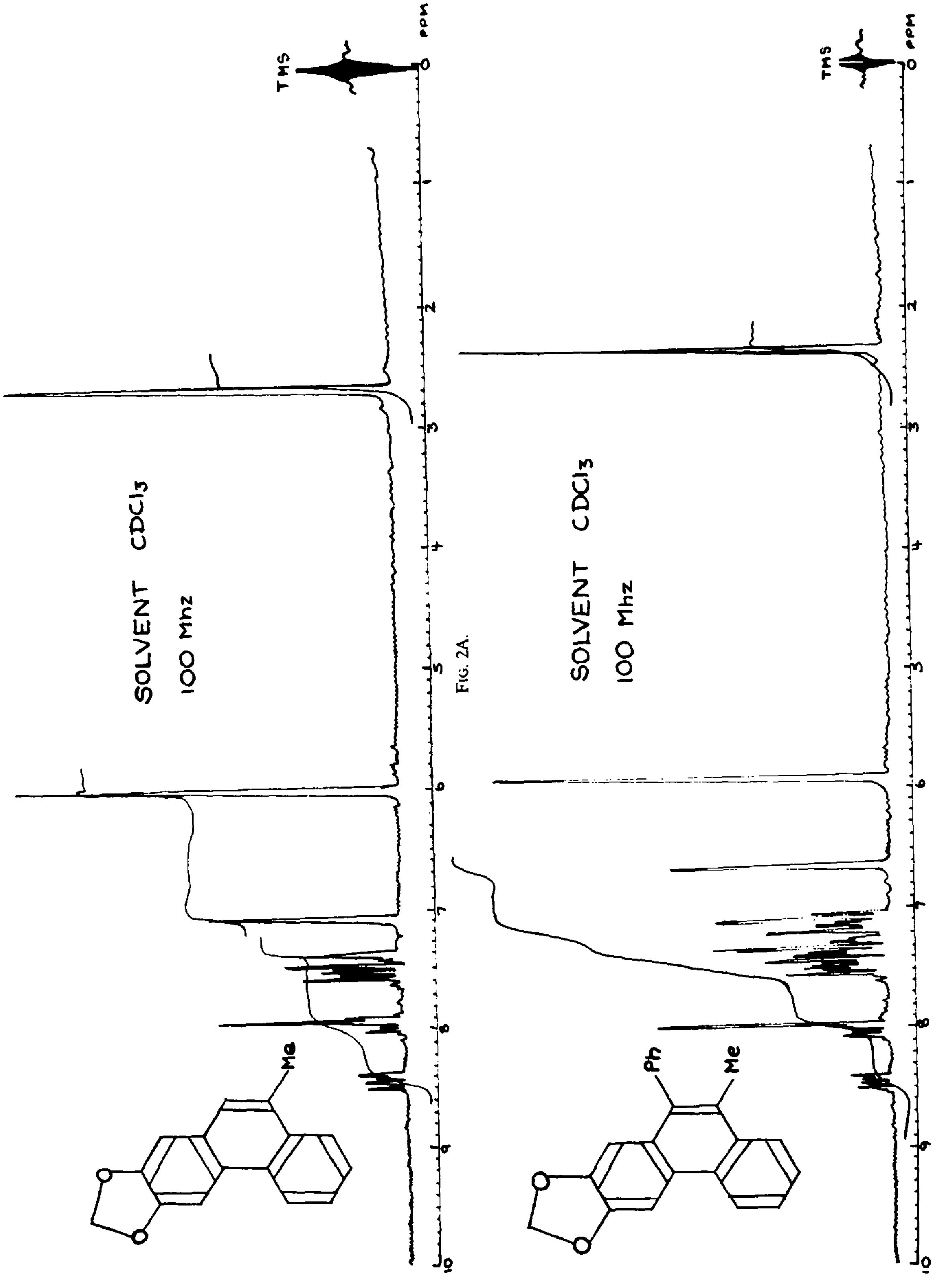
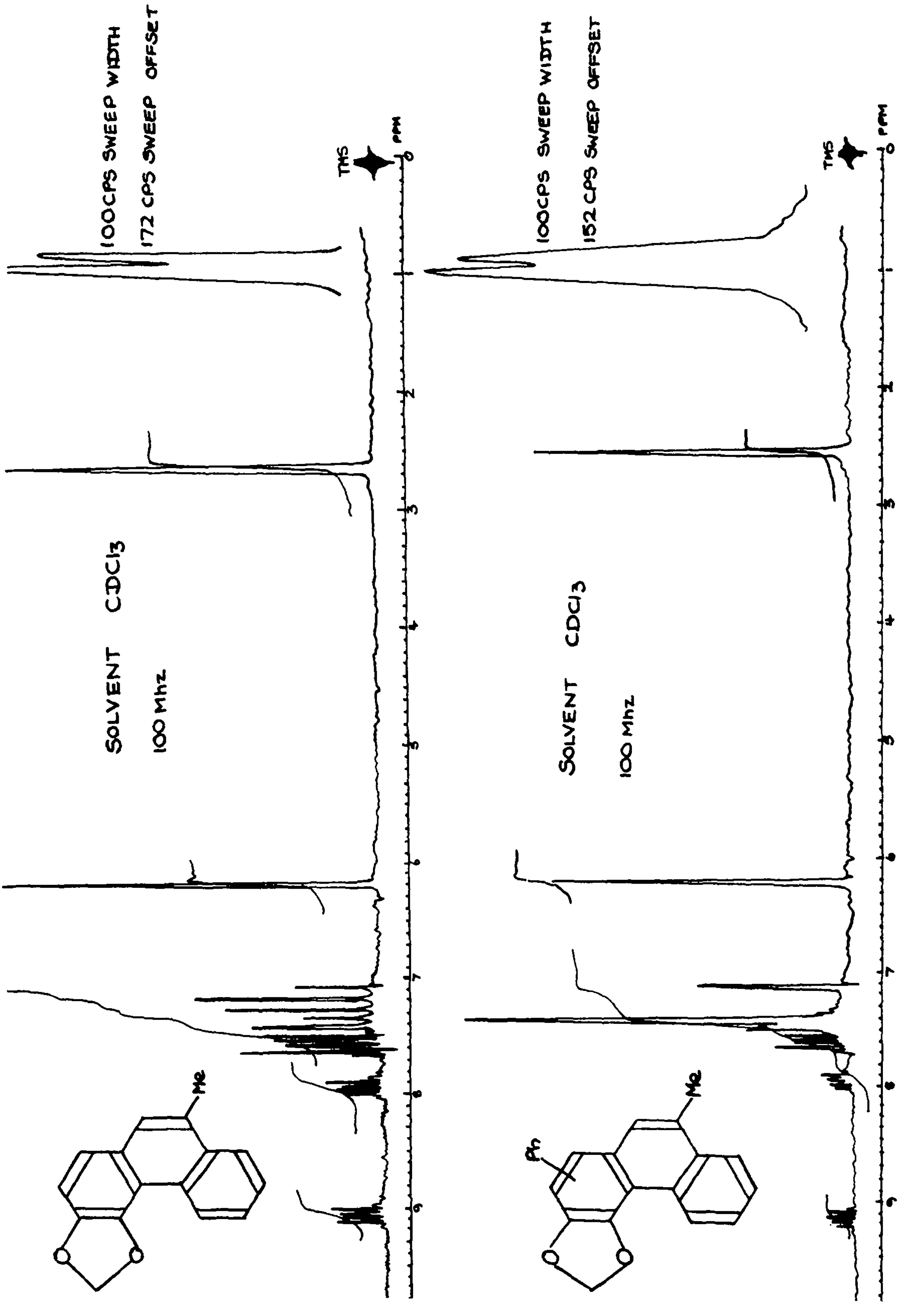

TMS
PPM
0
1
2
3
4
5
6
7
8
9
10
SOLVENT CDCl3
100 Mhz
Me
TMS
PPM
SOLVENT CDCl3
100 Mhz
Ph
Me

FIG. 2A.


100CPS SWEEP WIDTH
172 CPS SWEEP OFFSET
SOLVENT CDCl3
100 Mhz
TMS
PPM
Me
100CPS SWEEP WIDTH
152 CPS SWEEP OFFSET
SOLVENT CDCl3
100 Mhz
TMS
PPM
Ph
Me
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1
2
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8
9

FIG. 3.

6·66 and 6·64, 6·56 δ (J = 7·8 Hz) in the spectrum of **5**, assigned to the C_1 and C_2 protons, while this quartet is absent from the spectrum of **2b**, which has instead singlet peaks at 7·32 and 6·58 δ assigned to the C_4 and C_1 protons. It is interesting to note that in both these compounds the protons of the methylenedioxy group are non-equivalent.

The dihydroisocoumarin structures **6** and **7** were established from analytical and spectral data. The IR spectra exhibited strong carbonyl bands at 1720 cm^{-1}, and the molecular ions at m/e 282 in their mass spectra are in agreement with the required formula of $C_{17}H_{14}O_4$. The fragmentation patterns can be rationalized as shown in Fig 4.

The NMR spectrum of **6** exhibited a three proton doublet (J = 7·5 Hz) at 1·0 δ ($CH_3CH_A<$); a one proton multiplet (H_A) centred at 3·15 δ and a one proton doublet (H_B) at 5·6 δ (J = 3·0 Hz). The NMR spectrum of **7** is similar to that of **6** except that one proton doublet (H_B) at 5·08 δ has J = 9·5 Hz. The *trans* isomer **7** on treatment with

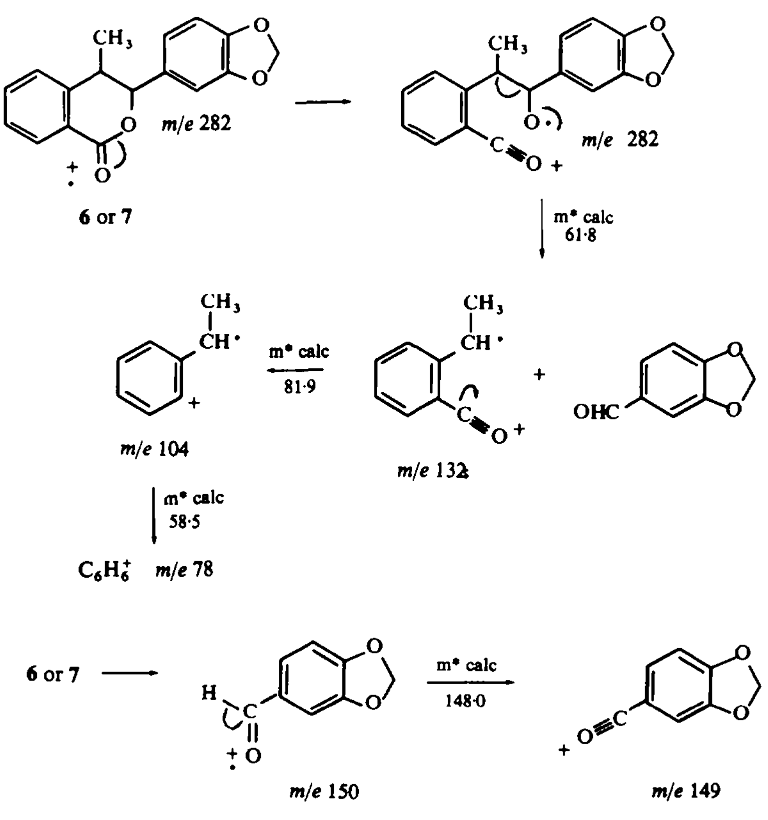


Fig. 4.

6 m/e (RI) 283(4·4) 282(24·8) 280(2·9) 150(1·8) 149(3·5) 148·0(m*) 133(10·3) 132(100) 131(5·1) 130·0(m*) 104(26·3) 103(7·3) 81·9(m*) 78(4·8) 77(4·4) 65(2·5) 63(3·0) 61·8(m*) 58·5(m*) 33·5(m*)
7 m/e (RI) 283(4·6) 282(25·5) 150(3·8) 149(7·0) 148·0(m*) 133(17·9) 132(100) 130·0(m*) 105(6·8) 104(62·0) 103(22·5) 81·9(m*) 78(18·3) 77(14·6) 76(4·6) 65(6·8) 63(9·1) 61·8(m*) 58·5(m*) 52(7·7) 33·5(m*)

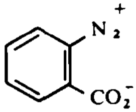
N-bromosuccinimide[11] in the presence of benzoyl peroxide, followed by dehydrobromination yielded the isocoumarin **10**, whose spectral characteristics are fully in accord with the structure assigned.

An additional compound, $C_{16}H_{14}O_2$, was isolated from the reaction between isosafrole and benzenediazonium-2-carboxylate hydrochloride. The presence of a vinyl group was indicated by bands at 928 and 1003 cm^{-1} in its IR spectrum, and this was confirmed by the appearance, in the NMR spectrum of the material, of a three proton complex absorption between 6·5–5·0 δ. The structure **8** for the compound was confirmed by catalytic hydrogenation when one mole of gas was absorbed to yield **9**, whose NMR spectrum is entirely in accord with this structure.

The original[1] reaction between isosafrole, anthranilic acid and amyl nitrite has been repeated, and in addition to the **1a**, **3** and acridone reported previously, compounds **2a**, **2b**, and **8** have been isolated in the yields indicated in Table 1.

When benzenediazonium-2-carboxylate (**11**) was decomposed at room temperature in the presence of isosafrole, the products obtained were the same as those described in the aprotic diazotisation experiment, and in about the same ratios. In our preliminary publication,[2] we suggested that the reduction in total yield in this experiment is due to a simple temperature effect. However, we have now repeated the reaction using boiling acetonitrile as solvent, and whilst the overall yield has been increased, the ratio of the products obtained has changed (Table 1). 2,3-Methylenedioxy-9-methyl-10-phenyl-9,10-dihydrophenanthrene (**2b**) is now the major product.

It is immediately evident from the above results that the mode of decomposition of benzenediazonium-2-carboxylate (**11**) closely parallels the behaviour of anthranilic acid when it is diazotised and heated in aprotic media, but that the properties of benzenediazonium-2-carboxylate hydrochloride (**12**) are quite different. In the first two cases, the losses of nitrogen and carbon dioxide, either occur simultaneously or follow one another very rapidly. The products obtained are then typically those expected from a benzyne intermediate. The formation of the dihydroisocoumarins (**6** and **7**), is consistent with loss of nitrogen from **12** to form[12] the ion **13**, which may either lose a proton and carbon dioxide to form benzyne, or may add to the double bond of isosafrole. More evidence for this stepwise decomposition of **12** to **13** has recently been provided.[13] It is possible that if a stronger base than propylene oxide were used, the life-time of **13**, and hence the yield of dihydroisocoumarins, would fall. Conversely, if diphenyliodonium-2-carboxylate which is known[12] to decompose in a stepwise manner through **13** is used as the benzyne precursor, the yields of isocoumarin derivatives might be increased to a synthetically useful level. This point is under investigation.



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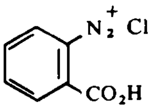

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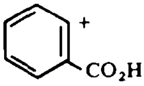

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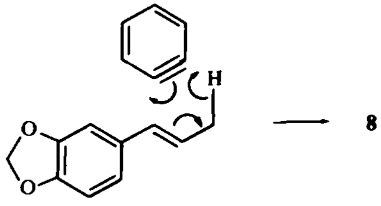
It has recently[14] been demonstrated that the benzyne generated from six different precursors, including the aprotic diazotisation of anthranilic acid and the thermal decomposition of benzenediazonium-2-carboxylate hydrochloride, has identical properties towards 1,4-dimethoxyanthracene. Presumably this diene does not act as a trap to the ion **13**, whereas isosafrole does.

The isosafrole used in all of the experiments described above was in fact a mixture containing 0·5% safrole, 18·5% *cis*-isosafrole and 81·0% *trans*-isosafrole. The recovered isosafrole from the reaction of method II contained 0·75% safrole, 23·4% *cis*-isosafrole and 75·9% *trans*-isosafrole (Experimental for details). The safrole derivative **8** clearly arises from the isosafrole and not from safrole in the starting material. The phenyl insertion product **8** may arise as indicated in **14**, but equally a proton transfer rather than hydride ion transfer may occur.



14

It seems that benzyne is acting as a dehydrogenating agent towards the 9-methyldihydrophenanthrene (**2a**), and in keeping with this, the proportion of this 9,10-dihydrophenanthrene to phenanthrenes is higher when the hydrochloride salt is used than it is in either of the other two methods of benzyne generation. On the other hand, the 9-methyl-10-phenyl-9,10-dihydrophenanthrene (**2b**) is very difficult to dehydrogenate and **1b** is only formed under the conditions of experiment IIIb. The 10-phenylphenanthrene derivatives might arise from **8** by isomerization and Diels–Alder addition to more benzyne, but it is more likely that phenyl insertion into the primary adduct **15** occurs. If this phenyl insertion is concerted, as established[7] for the addition of benzyne to styrene, the resulting dihydrophenanthrene (**2b**) should be the *trans*-isomer; unfortunately we have no conclusive evidence on this point. The phenyl insertion process is supported by the formation of **2b** as the major product when benzenediazonium-2-carboxylate (**11**) is decomposed in the presence of isosafrole in boiling acetonitrile, since the generation of benzyne is now rapid and may thus be trapped by **15**. As a corollary to this we would suggest that it is necessary for **15** to

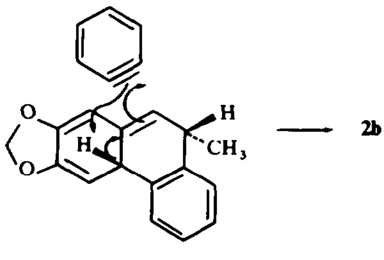


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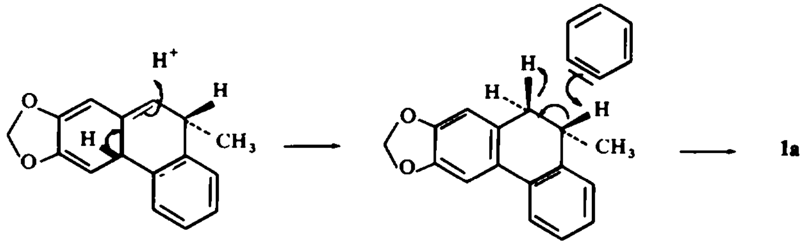
TABLE 2. GENERAL PHYSICAL PROPERTIES

Compound	m.p. °C	Cryst solvent	Molecular formula	Mass spectrum (M^+)	Found (%)		Required (%)		High resolution MS		Error (ppm)	Remarks
					C	H	C	H	Found	Required		
1a	139–141	EtOH	$C_{16}H_{12}O_2$	236	—		—		—	—		cf authentic sample[1]
1b	167–170	EtOH	$C_{22}H_{16}O_2$	312	84·80	5·41	84·59	5·16	0·114718	0·115023	−1·0	
2a	oil	—	$C_{16}H_{14}O_2$	238	—		—		—	—		cf authentic sample[1] converted → **1a**
2b	129–131	MeOH	$C_{22}H_{18}O_2$	314	83·81	5·82	84·05	5·77	—	—		converted → **1b**
3	107–108	EtOH	$C_{16}H_{12}O_2$	236	—		—		—	—		cf authentic sample[1]
4	131–132	EtOH	$C_{22}H_{16}O_2$	312	84·29	5·17	84·59	5·16	—	—		
5	143–144	EtOH	$C_{22}H_{18}O_2$	314	83·94	5·72	84·05	5·77	0·130800	0·130672	+0·4	
6	132–134	MeOH	$C_{17}H_{14}O_4$	282	72·61	5·26	72·33	5·00	—	—		IR ν_{max} C═O 1720 cm^{-1}
7	127–129	EtOH	$C_{17}H_{14}O_4$	282	72·48	4·82	72·33	5·00	—	—		IR ν_{max} C═O 1720 cm^{-1} converted → **10**
8	oil	—	$C_{16}H_{14}O_2$	238	—		—		0·098617	0·099373	−3·2	converted → **9**
9	oil	—	$C_{16}H_{14}O_2$	240	—		—		0·114434	0·115023	−2·5	
10	138–140	MeOH	$C_{17}H_{12}O_4$	280	—		—		0·073946	0·073552	+1·4	

rearrange to the 9,10-dihydrophenanthrene (**2a**) before dehydrogenation by benzyne can occur (**15** → **2a** → **1a**).



15 **2a**

TABLE 3. UV SPECTRA

Compound	λ_{max} nm (log ε)
1a	251 (4·63), 257 (4·66), 283 (4·29), 325 (3·34), 333 (3·11), 341 (3·53), 349 (3·10), 357 (3·59)
1b	253 sh (4·67), 258 (4·71), 277 (4·39), 283 (4·46), 326 (3·32), 333 (3·04), 341 (3·40), 349 (2·99), 353 (3·42)
2a	214 (4·61), 238sh (4·24), 282 (4·13) 292sh (4·04), 422 (4·10)
2b	214 (4·60), 237sh (4·28), 284 (4·00), 293sh (3·95), 322 (4·05)
3	215 (4·32), 241 (4·51), 249 (4·64), 257 (4·56), 285 (4·05), 316 (3·94), 354 (3·38), 372 (3·44)
4	225 (4·50), 240 (4·48), 254 (4·57), 266 (4·59), 290 (4·21), 330 (4·12), 360 (3·59), 379 (3·53)
5	234sh (4·17), 263sh (4·08), 272 (4·16), 284sh (3·97), 292 (3·77), 313 (3·50)
6	235 (4·16), 289 (3·79)
7	238 (4·20), 289 (3·93)
8	238 (3·92), 287 (3·71), 316 (2·99)
9	237 (3·47), 287 (3·39), 316 (2·63)
10	230 (4·36), 304 (4·10)

TABLE 4. NMR SPECTRA (60 MHz)

Compound	Chemical shifts in ppm from TMS internal standard
2a	7·7–7·4 [1H, m, Ar-H), 7·3–7·2 [4H, m, Ar-H], 6·76 [1H, s, C_1 or C_4–N], 5·84 [2H, s, O—CH_2—O], 3·2–2·4 [3H, m, C_9–H and C_{10}–H_2], 1·16 [3H, d, J = 6·5, C_9–CH_3]
6	8·25–8·08 [1H, m, C_8—H], 7·75–7·18 [3H, m, $C_{5,6,7}$—H], 7·05–6·84 [3H, m, $C_{2',5',6'}$—H], 5·95 [2H, s, O—CH_2—O], 5·65–5·58 [1H, d, J = 3, C_3—H], 3·25–2·92 [1H, m, C_4—H], 1·08–0·95 [3H, d, J = 7·5, C_4—CH_3]
7	8·25–8·07 [1H, m, C_8—H], 7·76–7·23 [3H, m, $C_{5,6,7}$—H], 6·95–6·8 [3H, m, $C_{2',5',6'}$—H], 5·94 [2H, s, O—CH_2—O], 5·13–4·98 [1H, d, J = 9·5, C_3—H], 3·54–3·06 [1H, m, C_4—H], 1·28–1·17 [3H, d, J = 7·5, C_4—CH_3]
8	7·25 [5H, s, C_3—Ph], 6·76–6·68 [3H, m, Ar—H], 6·45–6·00 [1H, m, C_2—H], 5·89 [2H, s, O—CH_2—O], 5·25–4·58 [3H, m, C_3—H and C_1—H_2]
9	7·25 [5H, s, Ar—H], 6·73 [3H, s, Ar—H], 5·82 [2H, s, O—CH_2—O], 3·92–3·58 [1H, t, J = 8·0, C_1—H], 2·25–1·76 [2H, m, C_2—H_2], 0·98–0·75 [3H, t, J = 8·0, C_3—H_3]
10	8·52–8·28 [1H, m, C_8—H], 7·96–7·38 [3H, m, $C_{5,6,7}$—H], 7·23–6·71 [3H, m, $C_{2',5',6'}$—H], 6·04 [2H, s, O—CH_2—O], 2·30 [3H, s, C_4—CH_3]

The remaining NMR spectra are reproduced in the text, i.e. Fig. 1 (**2b**, **5**), Fig. 2 (**1a**, **1b**), Fig. 3 (**3**, **4**).

It has recently been reported[7] that 9,10-dihydrophenanthrenes are not dehydrogenated by tetrahalogenobenzynes, but since the products obtained by the interaction of styrene with tetrafluoro- and tetrachlorobenzynes are different from those isolated when benzyne itself is used,[4] the discrepancy between this result and the interpretation we have placed on our results may not be fundamental. We are examining this point further.

EXPERIMENTAL

IR spectra were recorded for nujol mulls in the case of solids, or for thin films in the case of liquids, using a Perkin–Elmer 237 spectrophotometer. UV spectra were recorded for solns in EtOH, using Perkin–Elmer 137 or 402 spectrophotometers. NMR spectra were recorded for solns in $CDCl_3$ (TMS internal standard), using Varian A60 or HA 100 spectrophotometers. Mass spectra (70 eV) were recorded using A.E.I. MS 902 or MS 12 spectrometers.

Column chromatography and TLC was on silica gel. GLC was run on a Pye series 104 chromatograph, fitted with a hydrogen flame ionization detector and a 5 ft column (10% polyethylene glycol 20M on AW/HMDS treated 85–100 celite), % composition was determined by peak area.

The physical and spectral properties are tabulated in the text. M.ps are uncorrected.

Reaction of Isosafrole with Benzyne

Method I—Decomposition of benzenediazonium-2-carboxylate hydrochloride

A soln of isosafrole (48·9 g) and propylene oxide (28·5 ml) in acetonitrile (150 ml) was stirred and heated under reflux, whilst a slurry of benzenediazonium-2-carboxylate hydrochloride (36·9 g) in acetonitrile (400 ml) was added during 2½ hr. After further heating (2 hr) the solvent was removed under reduced press. A soln of the residual oil in ether was washed with 15% NaOHaq, water, dried ($MgSO_4$), and evaporated. Distillation under reduced press yielded isosafrole (30·1 g. 62%), followed by a dark orange oil (10·3 g), b.p. 117–200°/0·2 mm. This oil was fractionated by chromatography on a silica gel column, eluted successively with light petroleum (b.p. 60–80°)-benzene mixtures, benzene, and benzene–chloroform mixtures. The resultant fractions were treated by a combination of fractional crystallization and preparative TLC to yield the products listed in Table 1.

Compounds **2a** and **8** were not separated by TLC. GLC (220°, He flow 45 ml/min) gave **8** 24·5 min (21·4%) and **2a** 54·3 min (78·6%).

Method II—Aprotic diazotisation of anthranilic acid

A soln of isosafrole (69·6 g) in acetonitrile (250 ml) was stirred and heated under reflux, whilst solns of anthranilic acid (60 g) in acetonitrile (400 ml) and n-amyl nitrite (75 ml) in acetonitrile (125 ml) were added concurrently during 2½ hr. After further heating (2 hr) the soln was evaporated to ½ bulk and allowed to cool, when acridone (2·72 g) separated. The solvent was removed from the filtrate under reduced press and the residue dissolved in ether, when more acridone (0·77 g) separated. The ethereal soln was washed with 15% NaOHaq, water, dried ($MgSO_4$), and evaporated. After removal of a yellow solid (4·09 g), the residual oil was distilled under reduced press to yield isosafrole (43·7 g, 63%), followed by an orange oil (9·81 g), b.p. 160–198°/0·3 mm. Trituration of this oil with an ether–light petroleum (b.p. 30–40°) mixture yielded further pale yellow solid (4·20 g). The two solid fractions were combined and separated by preparative TLC, to yield compounds **1a** and **3**. The residual oil was fractionated and purified products isolated as in Method I. The total products isolated are listed in Table 1.

Compounds **8** and **2a** were not separated by TLC. GLC (220°, He flow 40 ml/min) gave **8** 25·1 min (92·8%), unknown compound (M^+ 238) 35·2 min (3·1%), **2a** 54·6 min (4·0%). The isosafrole recovered from the reaction was examined by GLC (160°, He flow 40 ml/min), found safrole 10·21 min (0·75%), *cis*-isosafrole 13·26 min (23·4%), *trans*-isosafrole 17·95 min (75·9%). This compared with isosafrole before reaction; safrole 10·20 min (0·5%), *cis*-isosafrole 13·21 min (18·5%), *trans*-isosafrole 17·92 min (81·0%).

Method III—Decomposition of benzenediazonium-2-carboxylate

(a) *At room temperature.* Benzenediazonium-2-carboxylate [prepared[3] from anthranilic acid (13·4 g)], isosafrole (29·7 g), and acetonitrile (500 ml) were stirred at room temp for 16 hr. After heating under relux for 2½ hr, the solvent was removed under reduced press. A soln of the residual oil in ether was washed with 15% NaOHaq, water, dried ($MgSO_4$), and evaporated. Distillation under reduced press yielded isosafrole

(19·7 g, 66%), followed by an orange oily solid (5·02 g), b.p. 106–236°C/0·2 mm. Fractionation by preparative TLC and recrystallization yielded the products listed in Table 1.

(b) *At the b.p. of acetonitrile.* A soln of isosafrole (29·2 g) in acetonitrile (250 ml) was stirred and heated under reflux, whilst an ice cold slurry of benzenediazonium-2-carboxylate [prepared[3] from anthranilic acid (16·4 g)] in acetonitrile (250 ml) was added during 1 hr. After further heating (2 hr), the solvent was removed under reduced press. The residual oil was treated in the manner of *Method IIIa* to yield isosafrole (16·3 g, 55%) and the products listed in Table 1.

Dehydrogenation of 2,3-*methylenedioxy*-9-*methyl*-9,10-*dihydrophenanthrene* (**2a**)

Compound **2a** (0·09 g) was heated under reflux in xylene (5 ml) with 5% Pd/C (0·5 g) for 48 hr. 2,3-Methylenedioxy-9-methyl-phenanthrene (**1a**) (0·085 g, 95%), m.p. 139–41° from EtOH, was produced. Identical (mixed m.p., IR, UV, MS) with authentic[1] sample.

Dehydrogenation of 2,3-*methylenedioxy*-9-*methyl*-10-*phenyl*-9,10-*dihydrophenanthrene* (**2b**)

A soln of **2b** (0·101 g) and tetrachloro-1,2-quinone (0·097 g) in xylene (3 ml) was heated under reflux for 34 hr, cooled, and the solvent removed under reduced press. A soln of the residue in ether was washed several times with 2% NaOH aq, water, dried ($MgSO_4$), and evaporated. Fractionation of the residue by preparative TLC yielded unchanged **2b** (0·008 g, 8%), and **1b** (0·040 g, 43%), colourless needles from EtOH, m.p. 167–170°. Identical with material isolated in *Method IIIb* above.

Dehydrogenation[11] *of trans*-3-(3′,4′-*methylenedioxyphenyl*)-4-*methyl*-3,4-*dihydroisocoumarin* (**7**)

Compound **7** (0·5 g), N-Bromosuccinimide (0·36 g), and benzoyl peroxide (0·005 g), in CCl_4 (15 ml) were heated under reflux for 1 hr, close to an illuminated 60-watt bulb. The orange colour, which developed, was discharged. Further benzoyl peroxide (0·005 g) was added and heating continued for 1 hr. The soln was cooled and filtered from succimmide, the filtrate and the washings were washed with 5% Na_2CO_3 aq, water, dried ($MgSO_4$), and evaporated. The colourless oily residue was heated under reflux with triethylamine (10 ml), after 24 hr further triethylamine (5 ml) was added and heating continued for 17 hr. Triethylamine was removed under reduced press. A soln of the residue in chloroform was washed with ice cold 2N HCl, water, dried ($MgSO_4$), and evaporated. Repeated purification by preparative TLC, followed by recrystallization from MeOH gave 3-(3′,4′-*methylenedioxyphenyl*)-4-*methyl-isocoumarin* (**10**), colourless prisms (0·185 g, 37%), m.p. 138–140°.

Hydrogenation of 3-*phenyl*-3-(3′,4′-*methylenedioxyphenyl*)-*prop*-1-*ene* (**8**)

Compound **8** (0·204 g, ~93% pure) in EtOH (5 ml) was hydrogenated at atm press and room temp in the presence of 10% Pd/C (0·044 g), when 90% of the theoretical amount of H_2 was absorbed. The soln was filtered and evaporated to leave a brown oil. After purification by preparative TLC, **9**, was obtained as a colourless oil (0·153 g, 76%). GLC (220°, He flow 40 ml/min) gave **9** 23·3 min (93·7%), unknown compound (M^+ 240) 27·3 min (3·6%), and **2a** 55·0 min (2·0%).

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